

Claims

1. A proton-conducting polymer membrane which comprises polyazole blends
5 and is obtainable by a process comprising the steps
A) preparation of a mixture comprising
polyphosphoric acid,
at least one polyazole (polymer A) and/or one or more compounds which are
suitable for forming polyazoles under the action of heat according to step B),
10 B) heating of the mixture obtainable according to step A) under inert gas to
temperatures of up to 400°C,
C) application of a layer using the mixture from step A) and/or B) to a support,
D) treatment of the membrane formed in step C) until it is self-supporting,
15 wherein at least one further polymer (polymer B) which is not a polyazole is
added to the composition obtainable according to step A) and/or step B) and
the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.
2. The membrane as claimed in claim 1, characterized in that the mixture
20 prepared in step A) comprises compounds which are suitable for forming
polyazoles under the action of heat in step B), with these compounds
comprising one or more aromatic and/or heteroaromatic tetraamino
compounds and one or more aromatic and/or heteroaromatic carboxylic acids
or derivatives thereof which have at least two acid groups per carboxylic acid
25 monomer and/or one or more aromatic and/or heteroaromatic
diaminocarboxylic acids.
3. The membrane as claimed in claim 1, characterized in that the mixture
30 prepared in step A) comprises compounds which are suitable for forming
polyazoles under the action of heat in step B), with these compounds being
obtainable by reaction of one or more aromatic and/or heteroaromatic
tetraamino compounds with one or more aromatic and/or heteroaromatic
carboxylic acids or derivatives thereof which have at least two acid groups per
35 carboxylic acid monomer or of one or more aromatic and/or heteroaromatic
diaminocarboxylic acids in the melt at temperatures of up to 400°C.
4. The membrane as claimed in claim 2 or 3, characterized in that aromatic
and/or heteroaromatic tetraamino compounds used as compounds suitable
for forming polyazoles comprise compounds selected from the group
consisting of 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and

1,2,4,5-tetraaminobenzene.

5. The membrane as claimed in claim 2, 3 or 4, characterized in that aromatic and/or heteroaromatic carboxylic acids or derivatives thereof having at least two acid groups per carboxylic acid monomer used as compounds suitable for forming polyazoles comprise compounds selected from the group consisting of isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides.
6. The membrane as claimed in claim 2, 3, 4 or 5, characterized in that the compounds suitable for forming polyazoles comprise aromatic tricarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides or tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides.
7. The membrane as claimed in claim 6, characterized in that the aromatic tricarboxylic acids comprise compounds selected from the group consisting of 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic acid.

8. The membrane as claimed in claim 6 or 7, characterized in that the content of tricarboxylic acid and/or tetracarboxylic acids is from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%, based on dicarboxylic acid used.
9. The membrane as claimed in one or more of claims 2 to 8, characterized in that the compounds suitable for forming polyazoles comprise heteroaromatic dicarboxylic acids, tricarboxylic acids and/or tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatics.
10. The membrane as claimed in claim 9, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid, and also their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides are used.
11. The membrane as claimed in claim 2 or 3, characterized in that the compounds suitable for forming polyazoles comprise diaminobenzoic acid and/or its monohydrochloride and dihydrochloride derivatives.
12. The membrane as claimed in claim 1, characterized in that the polymer B) is used in step A) in an amount in the range from 10 to 50% by weight, based on the weight of the mixture A) and/or B).
13. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polyolefin.
14. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-O bonds.
15. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-S bonds.
16. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one polymer having C-N bonds.

17. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one inorganic polymer.
18. The membrane as claimed in claim 1, characterized in that the polymer B) comprises at least one sulfonated polymer.
19. The membrane as claimed in one or more of the preceding claims, characterized in that the heating according to step B) is carried out after the formation of a sheet-like structure according to step C).
20. The membrane as claimed in claim 1, characterized in that the treatment according to step D) is carried out at temperatures in the range from 0°C to 150°C in the presence of moisture.
21. The membrane as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out for from 10 seconds to 300 hours.
22. The membrane as claimed in claim 1, characterized in that the membrane formed after step D) is crosslinked by action of oxygen.
23. The membrane as claimed in claim 1, characterized in that a layer having a thickness of from 20 to 4000 μm is produced in step C).
24. The membrane as claimed in claim 1, characterized in that the membrane formed after step D) has a thickness of from 15 to 3000 μm .
25. An electrode provided with a proton-conducting polymer coating which comprises polyazole blends and is obtained by a process comprising the steps
- A) preparation of a mixture comprising polyphosphoric acid, at least one polyazole (polymer A) and/or one or more compounds which are suitable for forming polyazoles under the action of heat according to step B),
- B) heating of the mixture obtainable according to step A) under inert gas to temperatures of up to 400°C,
- C) application of a layer using the mixture from step A) and/or B) to an electrode,
- D) treatment of the membrane formed in step C),
- wherein at least one further polymer (polymer B) which is not a polyazole is added to the composition obtainable according to step A) and/or step B) and

the weight ratio of polyazole to polymer B is in the range from 0.1 to 50.

26. The electrode as claimed in claim 24, wherein the coating has a thickness of from 2 to 3000 μm .

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27. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 24.

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28. A membrane-electrode unit comprising at least one electrode as claimed in claim 25 or 26 and at least one membrane as claimed in one or more of claims 1 to 24.

29. A fuel cell comprising one or more membrane-electrode units as claimed in claim 27 or 28.